DEACTIVATION OF PT-ZSM-5 FOR SELECTIVE REDUCTION OF NO

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INTRODUCTION
Recent reports suggest the use of Pt-ZSM-5 with hydrocarbons to reduce NO selectively under oxidizing conditions (1,2) and our laboratories, among others (3,4) are investigating the use of Pt-zeolites to reduce NOx in the emission of Diesel or gasoline lean-burn vehicles.   Here we consider the activity of Pt-ZSM-5, both as a fresh catalyst and after deactivation, and characterize a troubling aspect of catalyst deactivation. In severely deactivated materials, TEM reveals a film to have formed over Pt metal; we suggest this film is siliceous material derived from the zeolite and that an important mode of catalyst deactivation is due to geometric site blockage by this film.

EXPERIMENTAL
Pt-ZSM-5 catalysts, containing 0.50 wt%, 1.31 wt%, 2.52 wt%, 4.4 wt%, and 4.67 wt% Pt, were prepared using H-ZSM-5 supplied by PQ Corporation containing a Si/Al ratio of 30.5, tested using two test gases, and aged in the model gas mixture for one to fifty hours at 700 °C or 800 °C. One gas mixture included 700 ppmv NO, 3300 ppmv propene, 1000 ppmv CO, 330 ppmv H_2, 7.5% O_2, 20 ppmv SO_2, 10% H_2O, 10% CO_2. The other gas mixture was similar, consisting of 700 ppmv NO, 700 ppmv propene, 300 ppmv CO, no H_2, 20 ppmv SO_2, 7.5% O_2, 10% CO_2, and 10% H_2O. The automated gas delivery and data acquisition system used chemiluminescent NOx, NDIR CO and N_2O, FID hydrocarbon, and paramagnetic O_2 detectors to monitor catalyst activity. Catalyst performance is conventionally reported by % converted except for N_2O formation by NO reduction, which is more informative to express as % NO reduced to N_2O. One gram of 20-40 mesh granules were typically tested with GHSV of 110,000 hr^{-1}.   Inclusion or omission of 20 ppm SO_2 did not affect performance.   EXAFS and XANES were obtained using an *in situ* reactor described elsewhere (5) at Beamline X-18B of the National Synchrotron Light Source at Brookhaven National Laboratory. X-ray diffraction intensity data was obtained by standard procedures. TEM images were obtained using a JEOL 4000EX microscope with 1.8 Å resolution.

RESULTS AND DISCUSSION
Pt-ZSM-5 deactivates rapidly. We examined the catalyst with highest initial performance most extensively. Catalysts were subjected to catalysis at 700 °C and 800 °C using either synthetic gas blend for up to 50 hr with temperature ramps interspered to allow the monitoring of deactivation. Figure 1 shows NO reduction performance under three conditions. Curves labeled 700°C and 800°C show performance after aging the catalyst at those temperatures in the gas blend that included 3300 ppmv propene while the curve labeled 700 ppmv involved aging the catalyst at 700°C using 700 ppmv propene. When fresh or mildly aged, the catalyst reduces NO over a greater temperature range when 700 ppmv propene are present compared with 3300 ppmv.   When 3300 ppmv propene is present, an exotherm of over 200°C occurs after propene lightoff. The magnitude of this exotherm is sufficient to close the temperature window when hydrocarbon levels are high (6). Figures 1 and 2 show deactivation is more rapid at 800°C than at 700 °C. Deactivation proceeds more quickly when 3300 ppmv is used in the synthetic gas compared with 700 ppmv propene. For aging times greater than 20 hr, essentially no NO was reduced when 3300 ppmv propene was used.

Figure 2 shows deactivation for propene oxidation for experiments utilizing 3300 ppmv propene. Progressive deactivation occurs for both aging temperatures. The higher temperature aging is clearly much more severe.   For example, thirty hr aging at 800 °C is more severe than 50 hr aging at 700 °C. Deactivation is most rapid initially. Judging on the basis of T_{50} increases, Figure 2
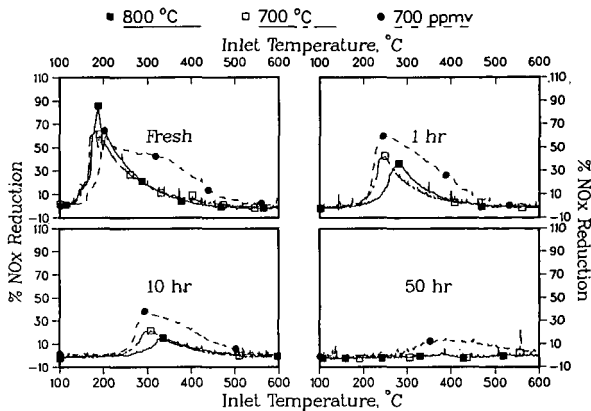
Figure 1. NO reduction, measured as conversion of NOx, deteriorates as aging proceeds. Higher temperature or higher propene concentrations accelerate deactivation.
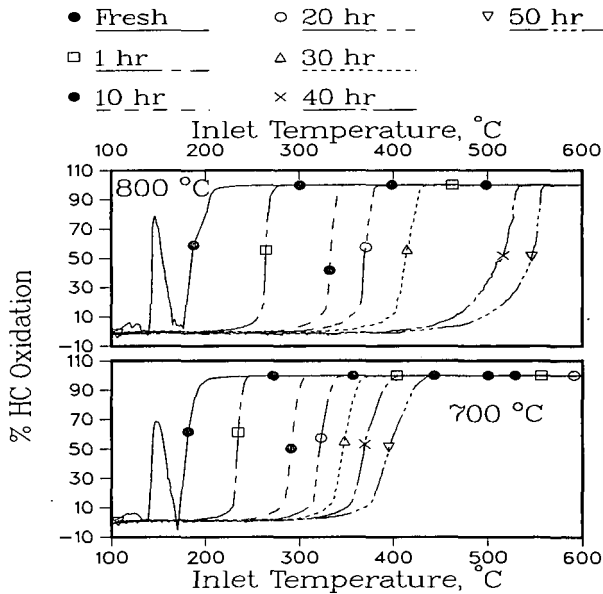

Figure 2. HC conversion progressively deactivates; 800 °C aging is much worse than 700 °C aging. Tests used 3300 ppmv propene.

shows performance losses during the first hour to be comparable to the next nine. The rate of HC deactivation slows to a nearly constant amount during the 700 °C aging. During 700 °C aging, the first 20 hr and the next 30 hr of aging resulted in T_{50} increases of about 100 °C for propene oxidation. At first glance, rates of HC deactivation do not appear to decline during the more severe 800 °C aging. However, an anomalously large incremental deactivation may have occurred between 30 and 40 hr during the high temperature aging. Comparable incremental deactivations occur between 10 and 20 hr, 20 and 30 hr, and 40 and 50 hr. These incremental deactivations at 800 °C are considerably larger than those observed at 700 °C, consistent with more severe, progressive deactivation at the higher temperature.

We now proceed to physical characterization to gain insight into deactivation prior to returning to the catalytic results.

TEM examination of fresh 4.7 wt% Pt-ZSM-5 reveals "stringy" regions, sometimes over 100 Å in length, of Pt. EXAFS and XANES analysis shows the Pt in fresh 4.7 wt% Pt-ZSM-5 to be oxidized. Metallic Pt is not detected by X-ray diffraction in the fresh material but is detected by XRD, EXAFS, and XANES after aging.

TEM analysis of catalysts aged at 800 °C for 1 hr or 50 hr also reveals Pt metal. After 1 hr, 800°C catalysis, faceted Pt particles occur, although many smaller Pt particles have poorly defined surfaces. Some particles are as large as 500 Å in diameter while particles about 100 Å appear most common. For example, one sector of a typical TEM micrograph contained 23 particles with a median diameter of 120 Å; mean diameter of 180 Å; with a range of diameters of 70 - 535 Å. Catalysts aged for 50 hr do not appear to be substantially more highly sintered. For example, one sector of a typical TEM micrograph of a sample aged for 50 hr contained 55 particles with a mean diameter of 100 Å, a median diameter of 70 Å; with a range of sizes from 40 - 400 Å. While Pt sintering may be the cause of the initial, rapid deactivation, the data do not support the hypothesis that the progressive deactivation we observe is due to continued sintering of Pt. While observable particles do not appear to be increasing in size, the TEM results do not exclude the possibility that the observable particles are increasing in mass. Small, unobservable, catalytically relevant Pt particles could persist as the aging proceeds, and their gradual loss may not cause noticeable increases in observable Pt particle sizes. Nevertheless, their gradual loss may be a cause of progressive deactivation if these postulated, unobservable entities are indeed catalytically relevant. CO dispersion measurements fail to provide evidence for the existance of the postulated small particles; CO isotherms of the aged materials are consistent with large particles whose surfaces, to a substantial degree, are inaccessible to the probe molecule.

Faceted Pt particles observed after 50 hr, 800°C catalysis frequently exhibit features consistent with a superficial film on their surfaces while these features are absent in the 1 hr samples. We suggest this film is due to silica or silica-alumina derived from the zeolite itself. This suggestion will be buttressed by a catalytic experiment discussed below. A surrendipitous TEM experiment performed on a Pt particle on the edge of a zeolite particle in a fresh sample provide corroborating evidence. This initially featureless Pt particle was is situated over a hole in the holey carbon TEM grid and, once noticed, was subjected to close-up examination using a more focused beam. Figure 3a and b show this particle as initially observed (but the image is enlarged photographically) and during high magnification TEM imaging (without photographic enlargement). Fringes consistent with (111) Pt domains are observed in Figure 3b while fringes due to crystalline zeolite (not observable in the small regions shown) vanish during focused beam exposure. A film of zeolite can be observed in the "northern" region of Pt in Figure 3b. The focused electron beam probably caused local heating that drove that region of the sample toward equilibrium: thermal reduction of oxidized Pt to Pt metal proceeded together with local amorphization of the zeolite. The zeolitic material spreading onto the Pt surface suggests that, as the catalyst approaches equilibrium at high temperature, siliceous films derived from the zeolite may cover otherwise active Pt metal. Films in severely deactivated materials manifest themselves as a white line, followed by a dark line, then followed by another white line at the edge of a Pt particle. Each solid-vacuum interface, under conditions of slight underfocus, should result in one white line. Pairs of parallel white lines are strong evidence of film formation. Such pairs of white lines are common at the Pt/vacuum surfaces in samples aged 50 hr at 800°C (for example, Fig. 3d) but only a single white lines are observed after 1 hr, 800°C aging (for example, Fig. 3c). Powell and Whittington used SEM to demonstrate Pt encapsulation by silica at temperatures of
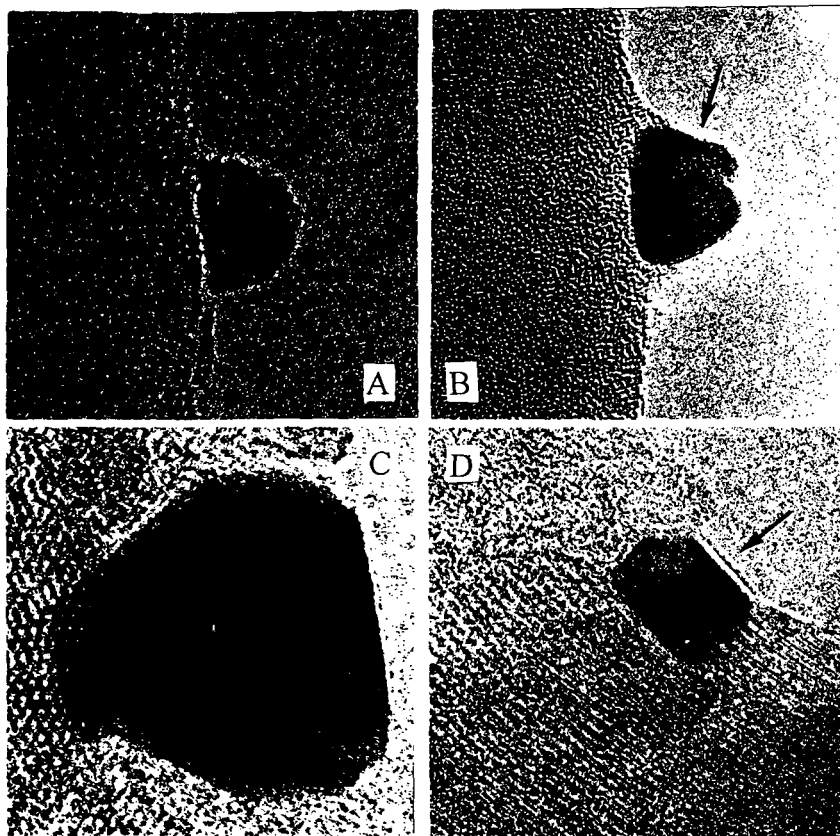
50 nm

Fig 3. (a) and (b) Pt particle and nearby zeolite in the fresh catalyst prior to (a) and after (b) beam damage. (c) Pt metal crystallite observed in sample aged 1 hr. (d) Pt metal crystallite, covered by superficial film, observed in sample aged 50 hr.

702 °C-1102 °C (7,8). Their model describing driving forces toward encapsulation appears to account for some of the phenomena we observe. Their model predicts encapsulated Pt particles will not tend to increase in size, as is observed here. Progressive catalytic deactivation should accompany progressive encapsulation. Figure 2 shows an increasing ΔT between the onset of propene conversion and the attainment of 25% conversion as deactivation proceeds. This steady increase in ΔT appears consistent with continually decreasing numbers of sites, just as an encapsulation model would predict. Successful development of durable Pt-molecular sieve catalysts requires additional understanding of this mode of deactivation that leads to effective countermeasures.

An alternate explanation of the films observed in the TEM invokes carbonaceous deposits formed by gradual coking of the catalyst. Oxidizing treatment might be expected to remove any such material. We aged the catalyst 50 hr in the gas blend containing only 700 ppmv propene. The rate of deactivation did decline, but since less propene is oxidized, temperatures at and near Pt might be

considerably lower than in experiments utilizing 3300 ppmv propene. After the aging, the catalyst was treated in 15.0% O_2/85.0% N_2 for one hour at 550°C. If the films were due to coking of Pt, this treatment should result in at least partial combustion of this film, and a concomittant increase in available Pt. A subsequent temperature ramp in the synthetic exhaust gas (700 ppmv propene) did not result in an increase in NO reduction. This is consistent with films arising from the parent zeolitic material, and not from the catalytic process. Efforts at further characterization of these films, such as TEM halography, are ongoing.

CONCLUSIONS

Fresh Pt-ZSM-5 shows reproducibly high degrees of NOx reduction in a narrow temperature window at very low temperatures. Initial performance is a function of Pt content: the more the better. NO selectivity toward N_2O is about 10%. Initially, Pt in the zeolite is oxidized but, apparently, not crystalline. A fraction of the Pt may occur as cations at exchange sites but relatively large (100 Å) Pt-containing particles occur. After one hour of lean-burn catalysis, the Pt is unambiguously metallic. The TEM-observable fraction of Pt may increase after reduction. Pt-ZSM-5 is not durable. After about 30 hr catalysis at AFR 22 and 800°C, no NOx reduction performance remains. NOx reduction is barely detectable (ca. 2% max.) after 40 hr catalytic aging at AFR 22 and 700 °C. Pt sinters; faceted 40-700 Å particles can be observed by TEM after 50 hr at 800 °C. While initial deactivation may be associated with moderate sintering of Pt, the unusual progressive deactivation is accompanied by formation of films on the Pt crystallites. We suggest these films are siliceous material derived from the zeolite itself and that the progressive deactivation is due to simple geometric site blockage.

Acknowledgements

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